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A muon spin relaxation study of the metal-organic magnet $Ni(TCNQ)_2$

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An investigation of the magnetism of the deuterated form of the metal-organic ferromagnet $Ni(TCNQ)_2$ using the muon spin relaxation technique, is reported. $Ni(TCNQ\text{-}D4)_2$ was synthesized in a similar manner to the protio-form, and the crystalline product formed was found to have a Curie temperature of $T_C = 20\,K$. This transition temperature was 18% larger than that of the protio-form synthesized in our laboratory. Muon spin relaxation measurements were performed in Zero Field (ZF) and in Longitudinal Fields (LF) of up to 0.45 T. The ZF data confirmed that the sample undergoes a bulk ferromagnetic transition at a temperature similar to that observed by the bulk magnetization data. However, ZF measurements also showed that another transition occurs below approximately 6 K, which is believed to be a transition to a magnetic glassy state. The LF results indicate that a significant dynamical component to the magnetism is present below T_C as LF fields up to 0.45 T cannot completely re-polarise the spins of the implanted muons. Moreover, at 5 mT, the data can be fit using a damped oscillatory function. Taken together, the ZF and LF results suggest the presence of two dominant sites for implanted muons, one of which is strongly coupled to the bulk magnetic transition and the other that is more weakly coupled and has a dynamical magnetic environment below T_C. Such a situation may be a consequence of muon spin relaxation probing core and surface magnetic environments of nanoparticles or clusters. *© 2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798616]

Organic based magnetism combines the areas of both chemistry and physics with the goal of creating tunable magnets where the T_C can be altered by simple changes to the organic moiety. By using a metal ion and creating a charge transfer salt with an organic radical acting as the anion, the organic can act as an exchange pathway between magnetic ions.[1,2] One of the first examples of charge transfer magnetic materials was the metallocene-TCNQ (7,7,8,8-tetracyanoquinodimethane) compounds, such as $[Fe(Cp^*)_2][TCNQ]$, which produced alternating stacks of electron donors (metallocene) and acceptors (TCNQ) where there was no direct bonding between the two. A T_C of 2.55 K was obtained from this compound.[3,4]

A further advancement in metal-organic magnetism was with the synthesis of the $M(TCNQ)_2$ series, where M = Fe, Mn, Co, and Ni.[5] These new compounds were unsolvated and there was clear evidence of crystallinity from x-ray diffraction data where the unit cell was predicted to be tetragonal. For the $Ni(TCNQ)_2$ compound, this showed a bulk ferromagnet transition with a $T_C = 20.8\,K$ ($\theta = 37\,K$); however, it is believed that there is a glassy component associated with the magnetic transition. The salt was produced from a metathesis reaction of a metal-acetronitrile tetrafluroborate salt and an ammonium TCNQ salt. Vickers *et al.* used a similar method where they produced amorphous, non-stoichiometric $M(TCNQ)_\gamma$ salts.[6] The Ni compound showed an elevated T_C of 31 K where the difference between the two procedures was instead of using a $[BF_4]^{2-}$ counter ion a weaker binding anion of $[SbF_6]^{2-}$ was used.

We report an investigation into $Ni(TCNQ)_2$ using muon spin relaxation (μSR), which is a powerful technique where one can study the local magnetism[8] within materials.[9] Our Zero Field (ZF) results suggest that there are two muon stopping sites; one that shows a strongly relaxing muon spin component and another with a slow, weak relaxation where, for the strong relaxing component, both a ferromagnetic transition and spin freezing are observed at two different temperatures. On application of a Longitudinal Field (LF), we observe a magnetic component that is transverse to the applied field indicative of hysteric behaviour within the sample.

Experiments were performed on a deuterated form of $Ni(TCNQ)_2$ (designated $Ni(TCNQ\text{-}D_4)_2$) using the EMU spectrometer at ISIS, UK. Deuteration was carried out to reduce the overall nuclear magnetic fields experienced by the implanted muons. $Ni(TCNQ\text{-}D_4)_2$ was synthesized using a similar method to Clérac *et al.*, but using $TCNQ\text{-}D_4$ which was produced using a method reported by Dolphin *et al.*[7]

The temperature dependent magnetization of $Ni(TCNQ\text{-}D_4)_2$ was measured with a Quantum Design MPMS using an applied field of 2.5 mT; the results are shown in Figure 1. Also included in the figure are data obtained from a $Ni(TCNQ)_2$ synthesized in our laboratory following the method of Clérac *et al.*[5] The magnetic measurements showed a difference in T_C of $\sim$3 K between the protio ($T_C = 17\,K$) and deutro ($T_C = 20\,K$) products. The divergence of the ZF cooled (ZFC) and field cooled (FC) curves show the

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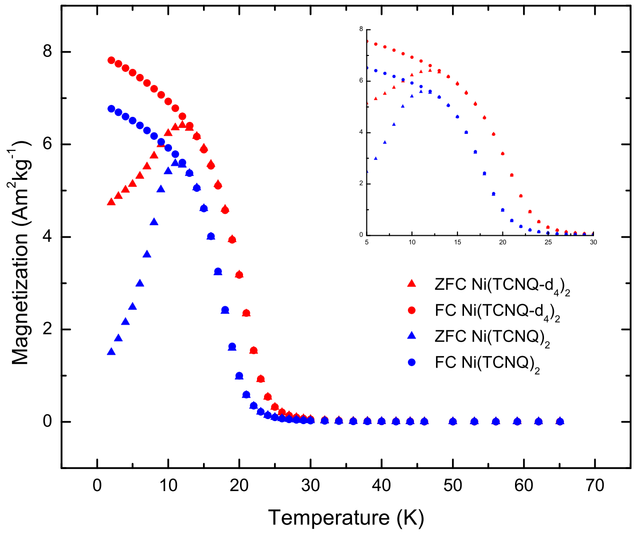

FIG. 1. Magnetization vs. temperature for the $Ni(TCNQ-H_4)_2$ and $Ni(TCNQ-D_4)_2$ products measured at 2.5 mT. At low T, the M changes slope which is possibly caused by the glassy behaviour of the material.

hysteresis present in the material at 2.5 mT. The divergence of the curves occurs at approximately 10 K and 12 K for $Ni(TCNQ)_2$ and $Ni(TCNQ-D_4)_2$, respectively.

A selection of ZF μSR spectra from $Ni(TCNQ-D_4)_2$, recorded at temperatures above and below T_C, are shown in Figure 2(a). At temperatures well above the T_C, the best fit to the data is using the sum of two gaussian relaxations[10] while at temperatures close to and below T_C, the data can be described well using a summation of two single exponential relaxations, suggesting two muon implantation sites

$$G(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) + A_{bg}, \quad (1)$$

where A_j corresponds to the asymmetry and A_{bg} accounts for muons stopping in the sample holder and cryostat. Note that no oscillatory component was observed in the raw ZF data below T_C. It is worthy of note that λ is the relaxation parameter, which is related to the internal spread of fields (Δ) as well as local fluctuations of the electronic moments; in the fast fluctuating limit $\lambda \propto \Delta^2/\nu$ where ν is the fluctuation rate. The total asymmetry and amplitude of the second component are shown in Figure 3(a) where a full asymmetry is recovered above the transition due to the internal fields within the sample no longer being motionally narrowed so the depolarisation of the muons occur in the measurable time scale. The increase in the total asymmetry as the sample is heated from 2 K supports a ferromagnetic transition with at $T_C \sim 20$ K. A_{bg} was fixed at 2.5% and it was found that the best fit to the data was when λ_2 was fixed at 0.03 μs^{-1} which describes a very slow relaxation that is not accounted for in the baseline.

The ZF relaxation parameter, λ_1, is shown in Figure 3(b) and the peak in the temperature response below 20 K indicating the magnetic transition. At lower temperatures (T $\leq$ 6 K), the value of λ_1 begins to rise and the asymmetry of component 2 also appears to exhibit a peak at around 4 K. From the magnetization data in Figure 1, at such low temperatures the ZFC curve changes slope and it may be that this deviation is associated with the glassy magnetic state reported by Clérac *et al.*[5]

The relaxation data shown in Figure 2(a) at $T > T_C$ (50 K), which is described by the sum of two gaussian terms, support the lower temperature results in suggesting that there are at least two muon stopping sites. In this higher temperature range, it is likely that the relaxation is due to nuclear dipolar fields associated with nitrogen atoms of the TCNQ molecule rather than the deuterium atoms. One can predict that the positively charged muon will be attracted to either the electron rich cyano-groups, where the radical is located on the TCNQ anion, or perhaps sit close to the π-electron density that exists above and below the TCNQ plane. To decouple this nuclear contribution, LFs of up to 0.45 T were applied. The LF acts to repolarise the muon spins previously depolarized by internal magnetic fields (both nuclear and electronic) weaker than the applied external field. We find that an optimal LF for decoupling the nuclear component is 5 mT. At higher LF values, a full muon spin repolarisation could not be achieved, even at fields of up to 0.45 T. This suggests that some muons are sensitive to slowly fluctuating magnetic moments and that there is a significant dynamical component of the magnetism present.[10]

In a LF of 5 mT, a damped oscillation was observed in the raw μSR data for $T < T_C$ (shown in Figure 2(b)) which was described at very short times by the function

$$G(t) = A_1 \exp(\lambda_1 t)\cos(\omega t + \phi) + A_2 \exp(\lambda_2 t) + A_{bg}. \quad (2)$$

The relaxation rate, λ_2 was fixed at 0.03 μs^{-1}, and A_{bg} was fixed at 2.5%. The oscillation frequency was also fixed at 0.6 MHz ($\sim$0.7 mT) which is related to the field

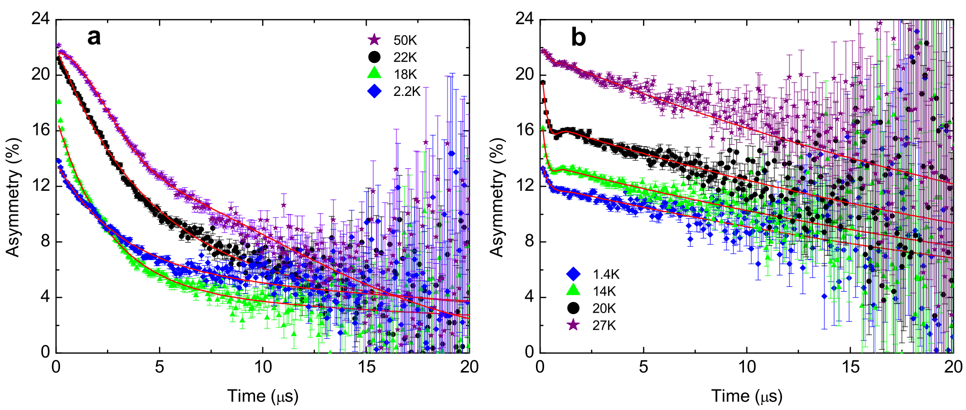

FIG. 2. (a) Zero field μSR raw data at selected temperatures above and below the magnetic transition. The solid lines are fits to the data. (b) Time dependent μSR spectra with a 5 mT LF where there is a complete decoupling of the nuclear component and the emergence of a heavily damped oscillation as T_c is approached. The lines are fits to the data using Eq. (2).

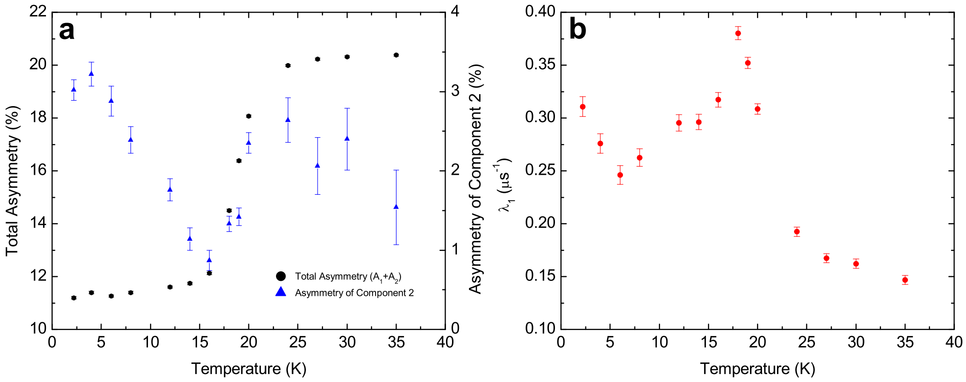

FIG. 3. (a) ZF asymmetry and the amplitude of component 2 (λ_2) showing the ferromagnetic transition at approximately 20 K. (b) λ_1 vs. temperature where there is evidence of a bulk transition similar to the magnetization data; however, at low temperature, another magnetic contribution appears.

experienced by the muon by $\omega = \gamma_\mu|\mathbf{B}|$, where γ_μ is the gyromagnetic ratio of the muon and $|\mathbf{B}|$ is the magnitude of the internal field experienced by the muon. It was also necessary to fix the phase, ϕ, at 0.12. The oscillation is an indication that there is a static internal field that has a component perpendicular to the initial muon polarisation. However, there is a strong dephasing of muons responding to this field as a second period of the oscillation is not observed and λ_1 for the LF data is an order of magnitude larger (e.g., $T = 15$ K, $\lambda_1 = 6\,\mu s^{-1}$) than that of the ZF relaxation. We conclude that an applied field of 5 mT not only repolarises muons that are dephased by the nuclear magnetic fields but also it appears to perturb the magnetism of the sample.

A possible interpretation of the different muon stopping sites indicated by the ZF data and the oscillatory behaviour of the LF = 5 mT data is that muons can implant in either the centre of a large ferromagnetic particle or in a region close to the surface of the particle. Also, the fact that the ZF data below 6 K support the presence of a possible magnetically glassy phase suggests a situation where the system is behaving either as a cluster glass or possibly nanoparticulate in nature. It may be possible that the nanoparticles are coupling through a dipolar mechanism at low T which would lead to an overall superspin glass state. Behaviour similar to that shown in Figure 3(b) has been observed in nanoparticle systems[11] and also cluster glasses.[12,13] If a muon were to stop in the centre of a particle/cluster, the internal fields may be very large and the muon spin would be depolarized rapidly and outside of the measurable time window at ISIS. If this was the case we would expect to see a 1/3 tail in the asymmetry that would correspond to the magnetic component aligned along the z-direction, or initial muon polarisation. Ultimately, the fixed λ_2 values may be the long time tail of this relaxation from the muons experiencing a very large internal field. A 1/3 tail is not present in our data and hence another relaxation process dominates in the majority of the muon decay within the ISIS time window. This may be associated with a muon stopping site which is close to the surface of, or in material between, the magnetic clusters/nanoparticles where the internal fields should be much weaker. The fact that λ_1 in ZF peaks close to T_C shows that these muons are still sensitive to the bulk magnetization of the ferromagnetic ordering in the material. However, the LF results demonstrate that there is a significant dynamical component to the magnetism. We note that the apparent onset of magnetic glassiness observed below 6 K may be due to the interaction of the magnetic particles where the system is behaving similarly to a super spin glass[14] or from behaviour similar to that of mictomagnetism (cluster glass).

In summary, we have shown that the deuterated and protio forms of $Ni(TCNQ)_2$ are ferromagnetic but with different Curie temperatures. Changes in T_C from isotope substitution have already been identified in different materials where there may be differences with electron-phonon coupling leading to subtle changes in the transition temperature.[15] μSR in $Ni(TCNQ\text{-}D4)_2$ was shown to be sensitive to the ferromagnetic phase transition close to 20 K but there was no evidence to suggest that this transition is accompanied by an onset to a magnetically glassy state. However, below 6 K, the ZF μSR data suggest the onset of a second magnetic state, which may be a glassy magnetic behaviour reported elsewhere,[5] but further measurements are needed below 2 K to confirm this conclusion. LF studies indicate the presence of nuclear magnetic fields, which can be decoupled in 5 mT. They also suggest that there are two muon sites in the material, which may be in the centre and at the surface of a ferromagnetic cluster/nanoparticle, and that fluctuations in the local magnetic fields are present even at temperatures well below T_C.

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